Exciton-relaxation dynamics in lead halides

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We survey recent comprehensive studies of exciton relaxation in the crystals of lead halides. The luminescence and electron-spin-resonance studies have revealed that excitons in lead bromide spontaneously dissociate and both electrons and holes get self-trapped individually. Similar relaxation has been also clarified in lead chloride. The electron-hole separation is ascribed to repulsive correlation via acoustic phonons. Besides, on the basis of the temperature profiles of self-trapped states, we discuss the origin of luminescence components which are mainly induced under one-photon excitation into the exciton band in lead fluoride, lead chloride, and lead bromide.

I. INTRODUCTION

Most of lead-compound crystals have the bandgap in connection with the 6*s*-to-6*p* gap in lead ions and tend to become highly luminescent coming from the 'odd' transition. In fact, excitonic transitions in lead halides are partly explained by the 6*s*-to-6*p* transition in lead ions [1, 2]. Luminescence in cubic PbF_2, $PbCl_2$, and $PbBr_2$ is composed of broad Gaussian bands with large-Stokes shifts and is indicative of strong exciton–acoustic-phonon interaction [1] while luminescence in PbI_2 shows free-exciton (FE) natures [3]. At the early stage of the study, the luminescence in lead halides was attributed to electric dipole transition from the 6*p* to 6*s* states [1, 4]. However, the description is too simple to explain the experimental results such as two-photon excitation spectra of photoluminescence (PL) [5, 6]. Cluster calculation for cubic PbF_2, $PbCl_2$, and $PbBr_2$ shows that the conduction bands consist of Pb^{2+} (6*p* states), and the top of valence bands is composed of 68% Pb^{2+} (6*s* states) and 32% F^- (2*p* states), 48% Pb^{2+} (6*s*) and 52% Cl^- (3*p*), and 35% Pb^{2+} (6*s*) and 65% Br^- (4*p*), respectively [2]. The tendency of the mixed ratio in the valence bands is qualitatively supported by the recent electron-spin-resonance (ESR) study manifesting self-trapping hole centers of Pb^{3+} in $PbCl_2$ [7] and ${Br_2}^-$ in $PbBr_2$ [8].

Mixed crystal of $PbI_{2(1-x)}Br_{2x}$ is an example to show the variety of exciton dynamics coming from lead-halogen complex; it enables us to observe the change from FE luminescence into self-trapped-exciton (STE) luminescence by increasing the ratio of bromide ions [9]. This system implies that halogen ions add the variety in exciton dynamics and play a crucial role in realizing the localization of excitons. This example tells us that the simple description based on the inner transition of lead ions is imperfect in discussing the lattice dynamics of excitons.

Moreover, it was recently reported that composite luminescence in $CsPbCl_3$, comprised of FE and STE luminescence, presents the recovery of FE-luminescence intensity and the sudden disappearance of the STE luminescence at a phase transition under the condition of raising temperature [10]; the excitonic transition stems from octahedrons of $Pb^{2+}(Cl^-)_6$, and the crystal has the valence and conduction bands similar to $PbCl_2$ [11]. Thus, lead-halogen complex makes it possible to realize a diversity of exciton relaxation.

We overview recent experimental results on $PbBr_2$ and $PbCl_2$ in the next section, and discuss the exciton relaxation resulting in spontaneous electron-hole separation in Sec. III. Furthermore, the properties of 'STE-like' luminescence in cubic PbF_2, $PbCl_2$, and $PbBr_2$ are examined from comparison with electronic localized states.

II. EXPERIMENTAL RESULTS: LEAD BROMIDE AND LEAD CHLORIDE

We mainly show optical and luminescent properties of $PbBr_2$ in this section because $PbBr_2$ and $PbCl_2$ are similar in the electronic-band structures [2] and luminescence properties [1, 6, 12]. Localized states of electrons and

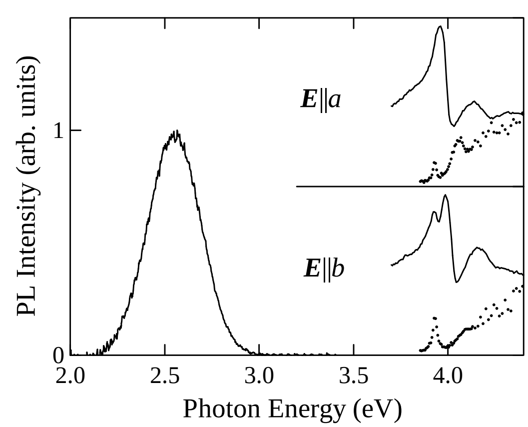

FIG. 1: Photoluminescence (PL) spectrum (left solid line), polarized reflectance spectra (right solid line), and two-photon excitation spectra (dots) of $PbBr_2$. All spectra were measured below 8 K. The PL was induced by 4.43-eV photons.

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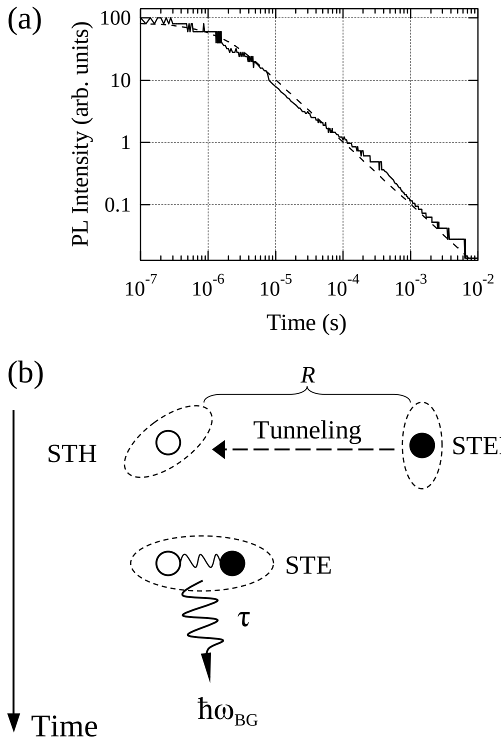

FIG. 2: (a) Decay curve (solid line) of PL in Fig. 1. (b) Recombination model that reproduces the decay curve; the calculated curve from the model is the dashed line in (a).

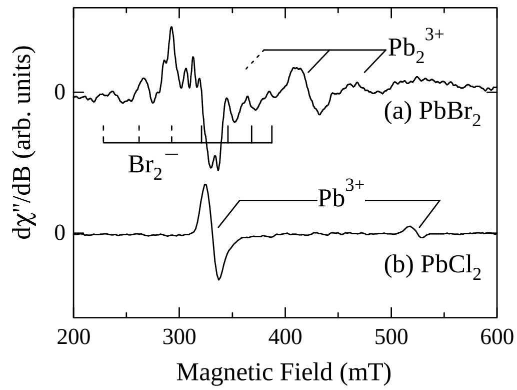

FIG. 3: Typical ESR spectra of (a) $PbBr_2$ and (b) $PbCl_2$ after photoirradiation below 8 K with 120-fs-width and 3.10-eV laser pulses. Both spectra were measured below 8 K. The resonant microwave frequencies were (a) 9.385 GHz and (b) 9.400 GHz. Solid lines indicate resonances, and dashed lines show the ESR positions calculated from the spin Hamiltonian in Ref. [8].

holes in $PbBr_2$ and $PbCl_2$ are also presented, which have been investigated with the ESR technique. More details of the luminescence spectroscopy and ESR study have already been reported in Refs. [5, 6, 7, 8].

Figure 1 shows photoluminescence (PL) spectrum (left solid line), reflectance spectra (right solid line) for $\mathbf{E}\|a$ and $\mathbf{E}\|b$ configurations, and two-photon excitation spectra (dots) of $PbBr_2$; all spectra were measured below 8 K. The PL at 2.55 eV was induced by 4.43-eV photons and is called blue-green-PL (BG-PL) band from now on. The two-photon excitation spectra indicate discrete peaks of exciton absorption at 3.93 and 4.07 eV, and the band edge is identified at 4.10 eV from the continuous rise. Consequently, the binding energy of the lowest exciton is estimated to be 170 meV. Similarly, the binding energy in $PbCl_2$ is found to be 200 meV [6].

Figure 2(a) presents a decay curve (solid line) of the BG-PL band in Fig. 1; the curve is plotted with the log-log scale. The intensity decays in proportion to $1/t$ for $t \geq 10$ μs. Such a decay curve cannot be explained by radiative transition in two-level systems but requires a process including tunneling motion [13]. Figure 2(b) depicts an electron-hole recombination model for the BG-PL band; a pair of a self-trapped electron (STEL) and a self-trapped hole (STH) separated by distance R gets close by tunneling motion, forms a STE, and recombines with the decay time τ. The τ was determined by time-resolved PL measurement in the microsecond range and is equal to 1.2 μs [5]. By assuming the distribution of pair density $n(R) \propto R^{-2}$, the model reproduces the measured decay curve well; the calculated curve is expressed as $I(t) = (A/t)[1 - \exp(-t/\tau)]$, where A is a proportionality constant, and is represented with the dashed line in Fig. 2(a). In $PbCl_2$, an intrinsic BG-PL band at 2.50 eV also shows a phosphorescent decay profile similar to the BG-PL band in $PbBr_2$ [6].

The recombination model hypothesizes the existence of STELs and STHs in $PbBr_2$. In fact, they are found in the ESR measurements as shown in Fig. 3; the ESR signals measured below 8 K were induced by photoirradiation below 8 K with pulsed 120-fs-width light at 3.10 eV, which induces two-photon interband transitions efficiently. Curve (a) in Fig. 3 presents the STEL centers of $Pb_2{}^{3+}$ and the STH centers of $Br_2{}^-$ in $PbBr_2$. The configurations of the STEL and STH centers were determined from the spin-Hamiltonian analysis of rotation-angle dependence of the ESR signals [8]; the dimer-molecular STEL centers orient along the a axis, and, on the other hand, the STH centers have two possible configurations in the unit cell, which are symmetric for the bc plane, reflecting the crystallographic symmetry. Experimental finding of coexistence of STELs and STHs is the first case to our knowledge.

Curve (b) in Fig. 3, which was measured like curve (a), shows the STH centers of Pb^{3+} in $PbCl_2$. Though the STEL centers of $Pb_2{}^{3+}$ in $PbCl_2$ were first observed after x- or γ-ray irradiation at 80 K [14, 15], the STEL centers are not detected at 0–1700 mT after photoirradiation below 50 K as shown in Fig. 3(b); indeed, the STEL centers of $Pb_2{}^{3+}$ appears thermally above 60 K [7]. If electrons below 50 K do form self-trapping centers of Pb^+ or $Pb_2{}^{3+}$, they could be detected in the range of

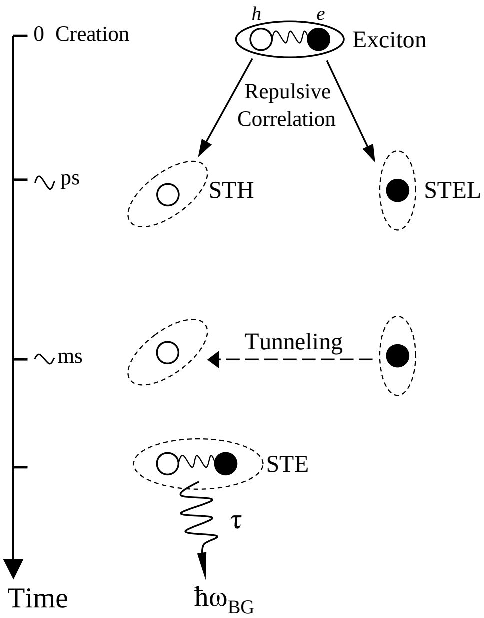

FIG. 4: Schematic description of exciton-relaxation dynamics in $PbBr_2$ and $PbCl_2$. In the latter crystal, the STEL has to be replaced with a trapped electron.

0–1700 mT because they usually have g values of 1–1.6 [14, 15, 16]. However, since they are not observed, other electron-trapping centers associated with lattice defects are most likely below 50 K.

Thermal stability of the STELs and STHs in $PbBr_2$ supports the correlation with the BG-PL band; in particular, the quenching of the STHs at 20–30 K corresponds to that of the BG-PL band. Thus, the STEs responsible for the BG-PL band are closely associated with the STHs.

The BG-PL band observed below 100 K in $PbCl_2$ corresponds to the STH centers of Pb^{3+} in the stable temperature range [7]. Therefore, the recombination model in Fig. 2(b) is applicable to the BG-PL band in $PbCl_2$ except for replacing the STEL with a trapped electron.

III. EXCITON RELAXATION IN LEAD HALIDES

Phosphorescent decay of the BG-PL bands in $PbBr_2$ and $PbCl_2$ is closely related to spatially separated electron-hole pairs as depicted in Fig. 2(b). However, can it happen that excitons with the binding energy of about 200 meV dissociate spontaneously?

Relaxed states of excitons were theoretically classified by Sumi [17]; as a result, excitons can relax into pairs of a STEL and a STH when both electrons and holes strongly interact with acoustic phonons. Particularly, when the signs of coupling constants of electron–acoustic-phonon and hole–acoustic-phonon interactions are opposite, repulsive force interplays between the electron and hole via acoustic phonons. Thus, the repulsive correlation is ascribable to the origin of electron-hole separation. Taking all the results and discussion into account, exciton-relaxation dynamics in $PbBr_2$ and $PbCl_2$ is schematically depicted in Fig. 4. The spontaneous breaking of initial bound states, namely excitons, takes place by the repulsive correlation via acoustic phonons; in view of bipolaron dynamics, the breaking is in contrast with the formation of Cooper pairs mediated by acoustic phonons.

Crystals	STEL	STH
Cubic PbF_2	×	Pb^{3+} [18]
$PbCl_2$	${Pb_2}^{3+}$ [14, 15]	Pb^{3+} [7]
$PbBr_2$	${Pb_2}^{3+}$ [8]	${Br_2}^{-}$ [8]
PbI_2	×	×

TABLE I: Structures of STEL and STH centers in lead halides. × denotes no report of self-trapping.

Table I summarizes the self-trapped states of excited electrons and holes. Self-trapping is observed in cubic PbF_2, $PbCl_2$, and $PbBr_2$; in particular, self-trapping of both electrons and holes is realized in $PbCl_2$ and $PbBr_2$. STHs in cubic PbF_2 irradiated with γ rays or neutrons were observed only at 77 K, and STELs were not detected at the temperature [18] though they might be observed at temperatures lower than 77 K.

From comparison with the stable temperature range of self-trapped states, we discuss another PL component induced mainly under excitation into the exciton band in each of PbF_2, $PbCl_2$, and $PbBr_2$. Figure 5 shows the PL bands (solid lines) and the excitation spectra (dashed lines) of $PbCl_2$ and $PbBr_2$ below 8 K; both of them appear in the energy range higher than the BG-PL bands. In cubic PbF_2, such a PL band appears at about 4 eV. The PL components have been assigned to STE lumines-

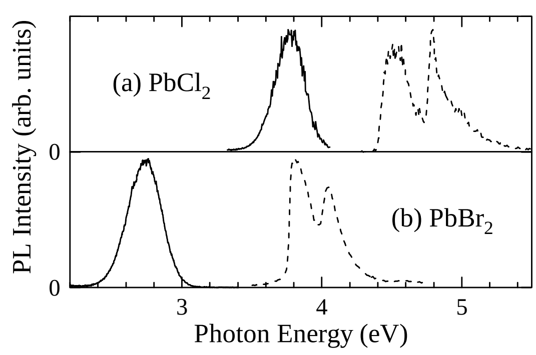

FIG. 5: (a) $PbCl_2$ and (b) $PbBr_2$: PL (solid lines) and the excitation spectra (dashed lines). All spectra were measured below 8 K. PL in (a) and (b) was induced by 4.80-eV and 3.81-eV photoexcitation, respectively. The excitation spectra were observed at (a) 3.76 eV and (b) 2.95 eV.

cence by many researchers [1, 12, 19, 20, 21, 22, 23]. However, the stable range disagrees with that of self-trapped states in each crystal: In cubic PbF_2, the PL component at 4 eV is quenched around 30 K [1, 21] while the STHs are bleached around 175 K [18]. In $PbCl_2$, the PL component at 3.8 eV disappears at 25 K [19, 20] while the STHs are stable up to 80 K and the STELs appear above 60 K [7]. In $PbBr_2$, the PL component at 2.7 eV disappears at 30 K while the STHs become unstable at 20 K and the STEL are stable up to 120 K [8]. In addition, the PL component is mainly induced under excitation into the exciton band while the STHs are induced also under interband excitation. Thus, all PL components attributed to STE luminescence show vital discrepancies with the STELs and STHs. If the PL components are intrinsic, the STEs responsible for the PL components need the different self-trapping centers from the STELs and STHs already detected with the ESR technique; however, further finding of the different self-trapping centers is quite improbable in these crystals.

To consider the origin of the PL component, we point out that cubic PbF_2 is a super-ionic conductor [24], and $PbCl_2$ and $PbBr_2$ are high-ionic conductors [25, 26]; therefore, they inevitably contain dense anion vacancies at higher than 10^{-17} cm^{-3}. In particular, lattice ions are absent with a high probability in the surface region because of the halogen desorption connected to the high-ionic conductivity. The vacancies may affect and trap the excitons induced by one-photon excitation only in the surface region. The excitation profiles of the PL components in the three crystals suggest that the excitons created by one-photon excitation behave similarly in the relaxation, and moreover the excitons are not coincident with any self-trapping center found experimentally to date. Therefore, the vacancy-associated relaxation of excitons seems to be a convincing explanation. At the end of discussion, we note that experimental data on cubic PbF_2 are partly inconsistent [1, 21]; the excitation profiles of PL component at 4 eV presented in the two references are different with each other. As for PbF_2, further study of luminescence and structures of localized states is necessary to clarify the exciton relaxation fully.

IV. CONCLUDING REMARKS

We have surveyed exciton relaxation in lead halides on the basis of recent experimental results. In $PbBr_2$ and $PbCl_2$, spontaneous exciton dissociation has been revealed with the luminescence spectroscopy and ESR technique. On the other hand, PbF_2 requires further investigation in view of luminescence properties and structures of localized states.

In cubic PbF_2, $PbCl_2$, and $PbBr_2$, the PL components with similar excitation profiles are discussed from the correlation with the STELs and STHs, so that they are inconsistent with any STEL and STH. Consequently, they are unlikely to be intrinsic. To identify the origins, the examination with the optically detected magnetic-resonance technique is most preferable.

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